

Chemical elements in the environment: Multi-element geochemical datasets from continental- to national-scale surveys on four continents



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ABSTRACT

During the last 10–20 years, Geological Surveys around the world have undertaken a major effort towards delivering fully harmonised and tightly quality controlled low-density multi-element soil geochemical maps and datasets of vast regions including up to whole continents. Concentrations of between 45 and 60 elements commonly have been determined in a variety of different regolith types (e.g., sediment, soil). The multi-element datasets are published as complete geochemical atlases and made available to the general public. Several other geochemical datasets covering smaller areas, but generally at a higher spatial density, are also available. These datasets may, however, not be found by superficial internet-based searches because the elements are not mentioned individually either in the title or in the keyword lists of the original references. This publication attempts to increase the visibility and discoverability of these fundamental background datasets covering large areas up to whole continents.

Keywords

Elements Ag (silver), Al (aluminium, aluminum), As (arsenic), Au (gold), B (boron), Ba (barium), Be (beryllium), Bi (bismuth), Br (bromine), C (carbon), Ca (calcium), Cd (cadmium), Ce (cerium), Cl (chlorine), Co (cobalt), Cr (chromium), Cs (caesium, cesium), Cu (copper), Dy (dysprosium), Er (erbium), Eu (europium), F (fluorine), Fe (iron), Ga (gallium), Gd (gadolinium), Ge (germanium), Hf (hafnium), Hg (mercury), Ho (holmium), I (iodine), In (indium), K (potassium), La (lanthanum), Li (lithium), Lu (lutetium), Mg (magnesium), Mn (manganese), Mo (molybdenum), N (nitrogen), Na (sodium), Nb (niobium), Nd (neodymium), Ni (nickel), P (phosphorous, phosphorus), Pb (lead), Pd (palladium), Pr (praseodymium), Pt (platinum), Rb (rubidium), Re (rhenium), S (sulphur, sulfur), Sb (antimony), Sc (scandium), Se (selenium), Si (silicon), Sm (samarium), Sn (tin), Sr (strontium), Ta (tantalum), Tb (terbium), Te (tellurium), Th (thorium), Ti (titanium), Tl (thallium), Tm (thulium), U (uranium), V (vanadium), W (tungsten), Y (yttrium), Yb (ytterbium), Zn (zinc), Zr (zirconium)

Properties Cation Exchange Capacity (CEC), Clay content, Electrical Conductivity (EC), Loss On Ignition (LOI), Magnetic Susceptibility, Mineralogy, pH, Sand content, Silt content, Total Carbon (TC), Total Inorganic Carbon (TIC), Total Organic Carbon (TOC)

Context Geochemistry, Geochemical Survey, Multi-Element, Regolith, Sediment, Soil

Location Australia, China, Europe, United States of America (USA)

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1. Introduction

Twenty years ago it was possible to summarise the sum total of large-scale geochemical survey data in a single book (Reimann and Caritat, 1997). Since then, there has been an explosion of geochemical surveys at the national, multi-national and even continental scales around the globe. These surveys have dominantly been fruits of the labour of Geological Surveys, and have been published in numerous atlases and/or survey reports. This large amount of data apparently has remained poorly visible to some segments of the research community. Three recent review articles on the occurrence and elemental cycles of specific chemical elements in the terrestrial environment (Tl and Cr - Karbowska, 2016; Belzile and Chen, 2017; Ertani et al., 2017) ignored or failed to find major existing, published and absolutely relevant datasets that would have provided the so urgently needed continental-scale background and context for such reviews. Four recent examples providing such data at the continental scale are the National Geochemical Survey of Australia (NGSA) project (Caritat and Cooper, 2011a), the China Geochemical Baselines (CGB) project (Zhang et al., 2012; Wang & CGB Sampling Team, 2015), the Geochemical Mapping of Agricultural and Grazing Land Soils (GEMAS) project in Europe (Reimann et al., 2014a, b), and the Soil Geochemical Landscapes (SGL) project of the conterminous United States (Smith et al., 2013, 2014) (Fig. 1). Numerous scientific journal articles on specific aspects of these four surveys have been published in addition to the original atlases/reports. This was pointed out in a 'Discussion' paper (Caritat and Reimann, 2017) to one of the above review articles, but again the concern is that this will not be 'visible' to authors around the world searching for specific keywords.

When three different groups of authors fail to find such fundamental datasets, it appears to be time to investigate what went wrong with the literature search process. Thus, the authors of this paper tried to find their own datasets on the internet starting from a single element like Tl or Cr and using variations of the search terms 'thallium', 'Tl', 'chromium', 'Cr', 'soil' and 'multi-element geochemistry', etc. It soon became clear that these datasets, although publicly available, will not appear on the first few screens of search results if one is not aware of the existence of these surveys and can start a more educated search for the datasets, e.g., using the project names.

One likely reason for the existing datasets published by the Geological Surveys being missed could be that all the element names/

symbols themselves never occur in the keyword lists of these publications, with the allowed number of keywords usually being limited. The aim of this communication is to overcome this shortcoming and increase the chances that future authors of review articles on specific elements in the environment discover the Geological Survey datasets from around the world during their internet searches.

2. Material and methods

2.1. The NGSA project

2.1.1. Introduction

The National Geochemical Survey of Australia (NGSA; www.ga.gov.au/ngsa) project (Caritat & Cooper, 2011a), a cooperation between the Federal and State/Northern Territory geoscience agencies in Australia, was part of the 5-year Onshore Energy Security Program managed at Geoscience Australia between 2006 and 2011 (Johnson, 2006). The NGSA was initiated to fill a significant knowledge gap about the composition of surface regolith at the continental scale by providing internally consistent pre-competitive data and knowledge to aid exploration for energy and mineral resources in Australia. Previously existing geochemical data in Australia were perceived to have limited spatial coverage, poor internal comparability and inadequate extent of reported elemental compositions (Caritat et al., 2008a). During a series of pilot projects that preceded the NGSA, a variety of sampling media, depth and grain-size fractions were tested at different sampling densities (Caritat et al., 2005, 2007, 2008b; Caritat and Lech, 2007; Lech and Caritat, 2007a, b). It was found that regolith samples collected on floodplains or similar low-lying landforms near the outlet of large catchments, or catchment outlet sediments, provided a suitable sampling medium for low-density geochemical mapping. These materials usually are a fine-grained mixture of detrital material originating from the main rock and soil types found within a catchment (Ottesen et al., 1989; Bølviken et al., 2004).

Many geochemical surveys have been carried out in Australia by Federal and State geoscience agencies, industry, and/or academic institutions (see below). Before NGSA, none was continental in scope mainly because a 'universal' sampling medium had not been recognised and also because of the perception that a relatively high sampling density was required, which would have been prohibitively expensive (L. Wyborn, pers. comm., 2003). Thus, the NGSA is the first local

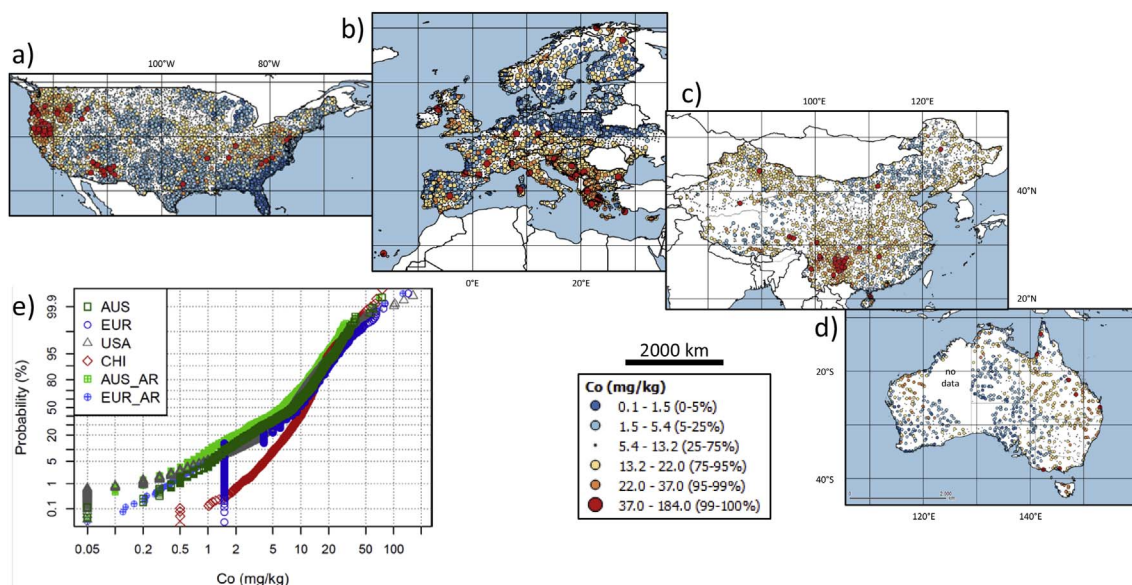


Fig. 1. Spatial distribution of total cobalt (Co) concentrations in soils over the four continental-scale geochemical projects (N = 11,617): (a) USA, (b) Europe, (c) China, and (d) Australia. Statistical distribution is also shown in the form of a quantile-probability plot, which also includes aqua regia Co (not mapped here) for Australia and Europe (e).

attempt at a uniform, internally consistent geochemical atlas and database using a common sampling medium, harmonised sampling protocols, and state-of-the-art, multi-element analytical equipment for an area in excess of 6,000,000 km² in extent. By necessity, the sampling density of NGSA was very low, on average 1 site per 5200 km², similar to the European Forum of European Geological Surveys (FOREGS) project (Salminen et al., 2005).

2.1.2. Sampling

Sampling took place during 2007–2009 and followed the detailed instructions within the NGSA field manual (Lech et al., 2007). Project staff travelled to each State/Northern Territory for a week-long training fieldtrip with the sampling teams from the local geoscience agency. All field equipment, including hardware and consumables (sampling bags, etc.) were purchased centrally and distributed to the field teams. The selected sampling medium was ‘catchment outlet sediment’ from floodplains or similar landforms located near the spill point or lowest point of large catchments. Here a surface (0–10 cm deep) ‘Top Outlet Sediment’ or TOS, and a deeper (on average 60–80 cm deep) ‘Bottom Outlet Sediment’ or BOS samples were collected. The more general terminology of ‘catchment outlet’ sediment was preferred to ‘floodplain’ or ‘overbank’ sediment to reflect the reality that in parts of Australia there will be an aeolian contribution to these surficial materials. Those samples also have been referred to as soils (‘topsoils’ and ‘subsoils’ generally representing the A and B/C or C horizons, respectively, where these are distinguishable) in some NGSA publication due to their being biologically and pedogenetically active (e.g., Caritat et al., 2011). Both samples were taken as composite samples either from a shallow ~1 m² soil pit (TOS) or from generally at least 3 auger holes within an area of ~100 m² (BOS). Where augering was not possible, soil pits were dug. Site descriptions, GPS coordinates and digital photographs were recorded in the field as were texture, dry (if possible) and moist soil Munsell colours and field pH (Cooper et al., 2010; Caritat et al., 2011). In total, 1315 TOS and 1315 BOS samples (including ~10% field duplicates) were collected from 1186 catchments. Randomised sample numbers were pre-allocated to each site. The average weight of a sample was 9 kg.

2.1.3. Sample preparation

All samples were prepared in a central laboratory (Geoscience Australia, Canberra). The samples were oven-dried at 40 °C, homogenised and riffle split into an archive sample for future investigations and an analytical sample for immediate analysis. The latter was further riffle split into a bulk subsample, a dry-sieved < 2 mm grain size fraction subsample and a dry-sieved < 75 µm grain size fraction subsample (Caritat et al., 2009). Each of these subsamples were further split into aliquots of specific weight as per analytical requirements.

2.1.4. Analyses and quality control

The analytical program for the NGSA project was extensive:

- bulk properties (pH of 1:5 soil:water slurries, here converted to pH CaCl₂ following Henderson and Bui (2002), electrical conductivity of 1:5 soil:water slurries, visible-near infrared spectroscopy and laser particle size analysis);
- total concentrations of 60 elements by X-Ray Fluorescence spectrometry (XRF) (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, S, Cl), total digestion (fusion followed by HF + HNO₃ digestion) followed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Ag, As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Te, Th, U, V, W, Y, Yb, Zn, Zr), or other specialised methods (fire assay followed by ICP-MS for Au, Pd, Pt; alkaline fusion followed by ion specific electrode for F; and aqua regia digestion followed by ICP-MS for Se);
- aqua regia soluble concentrations of 60 elements by ICP-MS (Ag, Al,

Table 1

List of chemical elements and bulk properties reported in the four continental geochemical surveys (Australia, China, Europe, and USA), together with analytical methods. For full details, including digestion and instrumentation, please refer to the original references (Australia - Caritat et al., 2010; Caritat and Cooper, 2011a; China - Zhang et al., 2012; Wang and CGB Sampling Team, 2015; Europe - Reimann et al., 2014a, b; USA - Smith et al., 2013, 2014).

Continent	Australia	China	Europe	USA
Project	NGSA	CGB	GEMAS	SGL
Parameter				
<i>Chemical Elements</i>				
Ag	TOT,AR,MMI	DCA	AR,MMI	MA
Al	XRF,AR,MMI	XRF	XRF,AR,MMI	MA
As	TOT,AR,MMI		XRF,AR,MMI	AAS
Au	FA,AR,MMI	AR	AR,MMI	
B	AR	DCA	AR	
Ba	TOT,AR,MMI	XRF	XRF,AR,MMI	MA
Be	TOT,AR	MA	AR	MA
Bi	TOT,AR,MMI	MA	XRF,AR,MMI	MA
Br		XRF	XRF	
C		COMB	EA	
Ca	XRF,AR,MMI	XRF	XRF,AR,MMI	MA
Cd	TOT,AR,MMI		AR,MMI	MA
Ce	TOT,AR,MMI		XRF,AR,MMI	MA
Cl	XRF	XRF	XRF	
Co	TOT,AR,MMI	MA	XRF,AR,MMI	MA
Cr	TOT,AR,MMI		XRF,AR,MMI	MA
Cs	TOT,AR,MMI	MA	XRF,AR,MMI	MA
Cu	TOT,AR,MMI	MA	XRF,AR,MMI	MA
Dy	TOT,AR,MMI		MMI	
Er	TOT,AR,MMI		MMI	
Eu	TOT,AR,MMI		MMI	
F	ISE		XRF	
Fe	XRF,AR,MMI,TTT	XRF,MA,CAL	XRF,AR,MMI	MA
Ga	TOT,AR,MMI	XRF	XRF,AR,MMI	MA
Gd	TOT,AR,MMI		MMI	
Ge	TOT,AR	MA	AR	
Hf	TOT,AR	MA	XRF,AR	
Hg	AR,MMI		AR,MMI	AR
Ho	TOT,AR			
I		AFC	XRF	
In	AR	MA	AR,MMI	MA
K	XRF,AR,MMI	XRF	XRF,AR,MMI	MA
La	TOT,AR,MMI		XRF,AR,MMI	MA
Li	AR,MMI	MA	AR,MMI	MA
Lu	TOT,AR			
Mg	XRF,AR,MMI	MA	XRF,AR,MMI	MA
Mn	XRF,AR,MMI	XRF	XRF,AR,MMI	MA
Mo	TOT,AR,MMI		XRF,AR,MMI	MA
N		COMB	EA	
Na	XRF,AR	MA	XRF,AR	MA
Nb	TOT,AR,MMI		XRF,AR,MMI	MA
Nd	TOT,AR,MMI		MMI	
Ni	TOT,AR,MMI		XRF,AR,MMI	MA
P	MMI,XRF	XRF	XRF,AR,MMI	MA
Pb	TOT,AR,MMI		XRF,AR,MMI	MA
Pd	FA,MMI		AR*,MMI*	
Pr	TOT,AR,MMI		MMI	
Pt	FA,MMI*		AR*,MMI*	
Rb	TOT,AR,MMI	XRF	XRF,AR,MMI	MA
Re	AR			
S	XRF	XRF	EA,XRF,AR,MMI	MA
Sb	TOT,AR,MMI		XRF,AR,MMI	MA
Sc	TOT,AR,MMI		XRF,AR,MMI	MA
Se	AR,MMI		AR,MMI	AAS
Si	XRF	XRF	XRF	
Sm	TOT,AR,MMI		MMI	
Sn	TOT,AR,MMI		XRF,AR,MMI	MA
Sr	TOT,AR,MMI	MA	XRF,AR,MMI	MA
Ta	TOT,AR*,MMI	MA	XRF,AR,MMI	
Tb	TOT,AR,MMI		MMI	
Te	AR,MMI*		AR,MMI	MA
Th	TOT,AR,MMI		XRF,AR,MMI	MA
Ti	MMI,XRF	XRF	XRF,AR,MMI	MA
Tl	AR,MMI	MA	AR,MMI	MA

(continued on next page)

Table 1 (continued)

Continent	Australia	China	Europe	USA
Project	NGSA	CGB	GEMAS	SGL
Parameter				
Tm	AR			
U	TOT,AR,MMI		XRF,AR,MMI	MA
V	TOT,AR,MMI		XRF,AR,MMI	MA
W	TOT,AR,MMI	MA	XRF,AR,MMI	MA
Y	TOT,AR,MMI		XRF,AR,MMI	MA
Yb	TOT,AR,MMI		MMI	
Zn	TOT,AR,MMI		XRF,AR,MMI	MA
Zr	TOT,AR,MMI	XRF	XRF,AR,MMI	
<i>Bulk Properties</i>				
CEC			STU	
Clay content	LPSA		MIRS	
EC	POT			
LOI	CAL	GRAV,CAL	COMB	
Mag Sus			SUS	
Mineralogy	VNIRS		MIRS	XRD
pH	Field,POT		POT	
Sand content	LPSA		MIRS	
Silt content	LPSA		MIRS	
TC				EA
TIC				XRD
TOC			EA	CAL

*All values below detection.

AAS: Atomic Absorption Spectrometry; AFC: Alkaline Fusion; AFS: Atomic Fluorescence Spectrometry; AR: Aqua Regia; CAL: Calculated; COMB: Combustion; DCA: Direct Current Arc; Emission Spectrometry; EA: Elemental Analyser; FA: Fire Assay; Field: Field pH test kit; GRAV: Gravimetry; ISE: Ion Specific Electrode; LPSA: Laser Particle Size Analyser; MA: Multi-Acid digestion; MIRS: Mid InfraRed Spectroscopy; MMI: Mobile Metal Ion⁺; POL: Polarography; POT: Potentiometry; STU: Silver-Thiourea extraction; SUS: Susceptibility meter; TIT: Titrimetry; TOT: Total digestion (fusion then digestion by HF + HNO₃); VNIRS: Visible Near InfraRed Spectroscopy; XRD: X-Ray Diffraction; XRF: X-Ray Fluorescence.

As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Re, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, U, V, W, Y, Yb, Zn, Zr);

- Mobile Metal Ion[™] (MMI) concentrations of 54 elements by ICP-MS (Ag, Al, As, Au, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn, Zr); and
- FeO by titrimetry (on a subset) and LOI by gravimetry (on a subset) or by difference (100% - sum of major oxides and main trace elements).

Bulk properties were determined on two subsamples at each site (TOS bulk and BOS bulk), whereas most other analyses were carried out on four subsamples at each site (TOS < 2 mm, TOS < 75 µm, BOS < 2 mm and BOS < 75 µm), except spectroscopic and MMI analyses, which were carried out only on TOS < 2 mm subsamples. Detailed method descriptions can be found in Caritat et al. (2010). The analytical methods for the elements/parameters used here are summarised in Table 1.

Quality control consisted of (1) randomised samples analysed in four large batches, (2) insertion of ~10% field duplicates, plus blind internal and exchanged project standards and blind Certified Reference Materials (CRMs). The results of quality control are reported by Caritat and Cooper (2011b). A recent review of NGSA research outputs was published by Caritat and Cooper (2016).

2.2. The CGB project

2.2.1. Introduction

The primary goal of the China Geochemical Baselines (CGB; [http://](http://www.globalgeochemistry.com/en/index.php)

www.globalgeochemistry.com/en/index.php) project (Zhang et al., 2012; Wang et al., 2015; Wang and CGB Sampling Team, 2015) was to provide high-quality geochemical concentration data and distribution maps for nearly all naturally occurring chemical elements over the whole of China in order to meet the growing requirements for geochemical information to aid in the sustainable development of natural resources and in protecting the environment. The resulting database and accompanying element distribution maps represent the current (2009–2012) geochemical baselines against which future human-induced or natural chemical changes can be recognised and quantified.

The CGB project was proposed in 2005, and started with a series of feasibility study meetings and workshops during 2005–2007, which aimed to develop the design for sample collection and to establish recommendations for sampling protocols, analytical methods, and data management. The project was formally launched in 2008. A 5-year term from 2008 to 2012 was financially supported by the Chinese government. The Ministry of Finance of the People's Republic of China provided the funding for this project. The Ministry of Land and Resources was responsible for project management. The coordinating organisations were the China Geological Survey and the Chinese Academy of Geological Sciences. The project was carried out by the Institute of Geophysical and Geochemical Exploration (IGGE) and the UNESCO International Center on Global-scale Geochemistry (ICGG). Sampling was completed in 2012 and laboratory analyses completed in 2014. Thirty nine of the 81 geochemical parameters are available now from the ICGG website (<http://www.globalgeochemistry.com/en/index.php>) and the other elements are expected to be released shortly when the CGB Atlas will be published.

2.2.2. Sampling

A total of 1500 grid cells were designed over the whole mainland China (9,600,000 km²). Each grid cell was 1 degree of longitude × 40 min of latitude or approximately equal to 80 × 80 km in size. The sample sites were selected from at least the two largest drainage catchments in each grid cell. Samples were taken from drainage catchments ranging in area from about 1000 to 5000 km², with most being 2000–3000 km² in area. Two samples were collected at each site: a top sample and a deep sample. The top samples were generally collected from the A horizon from a depth of 0–25 cm, or from the surface to the bottom of A horizon where the thickness of A horizon was less than 25 cm. The deep samples were generally collected from a depth of more than 100 cm where the top of the C horizon was deeper than 100 cm, or from the deepest possible part of the C horizon where the soil horizon was shallower. Samples were composited from generally three soil pits dug at the apices of a triangle with sides less than 50 m long. The weight of each sample was about 5 kg. The number of field duplicate samples exceeded 3% of the total number of samples. A total of 6617 samples from 3382 sites were collected at 1500 grid cells across the whole of China, corresponding to an average density of approximately one sample site per 3000 km².

The sampling methodology was developed and updated for China's diverse landscape terrains that include mountain, hill, plain, desert, grassland, loess and karst terrains in order to obtain high-resolution and harmonious nationwide baseline data. Floodplain sediment or alluvial soil was used as the sample medium in plain and hilly landscape terrains of exorheic river systems in eastern China. Overbank sediment was adopted as the sampling medium in mountainous terrains of exorheic river systems in southwestern China. Methods of collecting catchment basin and lake sediments were developed in desert and semi-desert terrains, respectively, in endorheic drainage systems in northern and northwestern China.

2.2.3. Sample preparation

After being air-dried and homogenised, each raw sample of 5 kg was split into two sub-samples, one of 2 kg, which was sieved to less than 10 mesh (< 2 mm) for laboratory analysis, and the other of 3 kg for

storage and future investigation. A 1 kg sieved sample was ground to less than 200 mesh ($< 74 \mu\text{m}$) in an agate mill. A 500 g ground sample split was sent to the laboratory for analysis; the other 500 g sample split was placed in a polypropylene bottle and stored in the sample archive room.

2.2.4. Analyses and quality control

Eighty-one geochemical parameters (76 chemical elements Ag, As, Au, B, Ba, Be, Bi, Br, Cd, Cl, Co, Cr, Cs, Cu, F, Ga, Ge, Hf, Hg, I, In, Ir, Li, Mn, Mo, N, Nb, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Zn, Zr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, SiO_2 , Al_2O_3 , Total Fe_2O_3 , MgO, CaO, Na_2O , K_2O , C, plus Fe^{2+} , Organic C, CO_2 , H_2O^+ , pH) were determined by ICP-MS/AES following 4-acid digestion and XRF on fusion beads as fundamental methods combined with 10 other methods (see Table 1). The details were described by Zhang et al. (2012).

The standardized quality control (QC) procedures consisted of: 1) field training for all sampling participants; 2) field sampling checking by random selection over 5% of total number of the sampling sites; 3) collection of 3% field duplicate samples; 4) blank insertion of 10% laboratory replicate samples; and 5) insertion of 4 standard reference materials into each batch of 50 routine samples (Wang et al., 2015).

2.3. The GEMAS project

2.3.1. Introduction

Geochemical Mapping of Agricultural Soils (GEMAS; <http://www.eurogeosurveys.org/projects/gemas/>) is a cooperation project between the Geochemistry Expert Group of EuroGeoSurveys (EGS) and Eurometaux. The GEMAS project was started to produce soil geochemistry data at the continental scale consistent with REACH (Registration, Evaluation and Authorisation of Chemicals - EC, 2006). REACH specifies that industry must prove that it can produce and handle its substances safely. Risks due to the exposure to a substance during production and use at the local, regional and European scale all need to be assessed. Industries handling metals needed harmonised data on the natural distribution of chemical elements and of the soil properties determining metal availability in soils at the continental scale. REACH requires that risk assessment is done according to land use. Early on in the planning stage of the GEMAS project it was decided to focus on agricultural and grazing land soils, both providing a direct link to the human food chain. According to REACH, the sample depth should be 0–20 cm for agricultural soils and 0–10 cm for grazing land soils and the grain size fraction to be analysed is the $< 2 \text{ mm}$ fraction. With the exception of the sample density, the framework for the project was thus rigidly fixed by external requirements. Forest soils are covered by the ICP-FOREST programme (<http://icp-forests.net/>) and related activities.

2.3.2. Sampling

Sampling took place during the year of 2008 according to a joint field manual (EGS, 2008). Project participants met in March 2008 in Berlin for a field training course. Here all participants were also equipped with the material needed for sampling (EGS, 2008). In short, two different sample materials were collected: (1) agricultural soils on regularly ploughed land to a depth of 20 cm (A_p -horizon, hereafter Ap) and (2) grazing land soil (land under permanent grass cover) to a depth of 10 cm. Samples were taken as composite samples from five pits within an area of $\sim 100 \text{ m}^2$. At one of the five pits, a soil profile was dug down to the next horizon and photographed. In total 2211 samples of agricultural soils and 2118 samples of grazing land soil were collected during 2008 (including $\sim 5\%$ field duplicates). The average weight of a sample was 3.5 kg.

2.3.3. Sample preparation

All samples were prepared in a central laboratory (Geological

Survey of the Slovak Republic). The samples were air dried and sieved to pass a 2 mm nylon screen. All samples were then randomised and analytical duplicates and project standards were introduced at a rate of 1 in 20. All samples were then split into ten aliquots using a Jones riffle splitter. Four splits of $\sim 200 \text{ g}$ each went to storage for later reference and six splits of 50–100 g each were sent to the different contract laboratories for the immediate analytical work.

2.3.4. Analyses and quality control

The analytical program for the GEMAS project was extensive:

- 53 chemical elements in an aqua regia extraction by ICP-MS (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr),
- total concentrations of 43 chemical elements/oxides by XRF (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO, MgO, CaO, Na_2O , K_2O , P_2O_5 , SO_3 , Br, Cl, F, I, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn, Zr);
- loss on ignition (LOI), total C, N and S, total organic carbon, cation exchange capacity (CEC) and pH in a 0.01 M CaCl_2 solution;
- Mid InfraRed (MIR) spectroscopy for all samples to build European soil models for the prediction of a number of soil properties; and
- soil adsorption coefficients (K_d) for 14 elements (Ag(I), B, Co(II), Cu (II), Mo(VI), Mn(II), Ni(II), Pb(II), Sb(V), Se(VI), Sn(IV), Te(VI), V (V), Zn(II)).

Quality control consisted of (1) randomization of all samples into one large batch for each material (Ap and Gr), (2) insertion of blind project standards and blind analytical duplicates at a rate of 1 in 20, and analyses of all samples for any given set of elements/parameters in one laboratory in a short time frame (e.g., aqua regia analyses completed in 20 days). Detailed method descriptions and results of quality control can be found in Reimann et al. (2009, 2011, 2012a). The two project standards Ap and Gr underwent an international ring test. Reference values for the two GEMAS project standards, allowing to judge the closeness of the GEMAS project analytical results to the 'true' values are provided in Reimann et al. (2012a, 2014a).

2.4. The SGL project

2.4.1. Introduction

In 2001, the Directors of the U.S. Geological Survey (USGS), the Geological Survey of Canada, and the Mexican Geological Survey (Servicio Geológico Mexicano) jointly recognised the need to establish a soil geochemical database for the continent of North America. These three agencies subsequently established the North American Soil Geochemical Landscapes Project (NASGLP; https://minerals.cr.usgs.gov/projects/soil_geochemical_landscapes/) to address this issue. A workshop was held in 2003 to obtain stakeholder input on the project's optimal design; it attracted 112 attendees representing 42 different stakeholder entities. One outcome of the workshop was a set of recommendations for sample collection protocols and analytical techniques for the proposed continental-scale soil geochemical survey. Smith et al. (2011a, 2012) document the history and evolution of the project from 2001 to 2010. Pilot studies were carried out from 2004 to 2007 to test and refine the sampling and analytical protocols developed at the 2003 workshop and to optimize field logistics.

Sampling for the full national-scale soil geochemical survey of the conterminous United States began in 2007 and was completed in 2010. Chemical analyses of the samples were completed in May 2013. Unfortunately, Canada dropped out of the project in 2009. At this time, the name of the U.S. portion of the project was changed to the Soil Geochemical Landscapes of the Conterminous United States (SGL; https://minerals.cr.usgs.gov/projects/geochemical_landscapes/index.html) and this terminology will be used throughout this paper. Mexico

has completed all sampling and chemical analysis, but has not yet made their data available to the public.

2.4.2. Selection of sampling sites

The SGL Project used a generalized random tessellation stratified (GRTS) design to select target sites that represent a density of approximately one site per 1600 km² (4857 sites for the conterminous United States). The GRTS design produces a spatially balanced set of sampling points without adhering to a strict grid-based system. Its attributes have been fully described in technical publications (Stevens and Olsen, 2000, 2003, 2004), and routines for implementing the design are readily available. If a target site was inaccessible for any reason during the sampling program, the field crew would select an alternative site as close as possible to the original site with the landscape and soil characteristics as similar to the original site as possible. The following guidelines were also used in the site selection process to ensure that samples were not collected from obviously contaminated areas:

- no sample should be collected within 200 m of a major highway;
- no sample should be collected within 50 m of a rural road;
- no sample should be collected within 100 m of a building or structure; and
- no sample should be collected within 5 km downwind of active major industrial activities such as power plants or smelters.

2.4.3. Sampling

Participants in the 2003 workshop (Smith et al., 2012) recommended that sampling at each site should be based primarily on soil horizons rather than on constant depth intervals. Sampling by horizon provides data on discrete soil genetic units, whereas depth-interval sampling mixes different genetic units in an uncontrolled and largely unknown manner. Stakeholders from the public health sector, however, strongly supported collection of surface soil from a depth of 0–5 cm because it is the portion of the soil profile which humans most often come into contact with during their daily activities.

The final protocols used for the national-scale survey were a combination of depth-based and horizon-based sampling. Ideally, the following samples were collected at each site: (1) soil from a depth of 0–5 cm; (2) a composite of the soil A horizon (the uppermost mineral soil); and (3) a sample from the soil C horizon (generally partially weathered parent material) or, if the top of the C horizon was deeper than 1 m, a sample from about 80 to 100 cm.

2.4.4. Sample preparation

All samples were shipped to the USGS laboratories in Denver, Colorado, where they were prepared and submitted for analysis by a USGS contract laboratory in the order they were collected, by state. As a result of this process, chemical analyses were carried out from late 2007 to early 2013. For large geochemical surveys like this one, the ideal course of action is to submit the samples for chemical analysis in a single batch after all samples have been collected in order to avoid bias in the chemical data caused by changes during the several years of the collection phase, such as changes in analytical instruments or analysts. The year-to-year budget process in the USGS, however, dictated that samples had to be submitted on a yearly basis. All samples within a given state were randomised prior to chemical analysis to avoid confusing spatial variation with any possible systematic bias within a given analytical technique. This randomization does not eliminate a systematic error, but the error is effectively transformed into one that is random with regard to geographic location within a state. Each sample was air-dried at ambient temperature, disaggregated, and sieved to < 2 mm. The < 2 mm material was then crushed to < 150 µm prior to chemical analysis.

2.4.5. Analyses and quality control

The analytical program included the following for all three sample

types:

- concentrations of 41 elements (Al, Ca, Fe, K, Mg, Na, S, Ti, Ag, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Ga, In, La, Li, Mn, Mo, Nb, Ni, P, Pb, Rb, Sb, Sc, Sn, Sr, Te, Th, Tl, U, V, W, Y, Zn) by ICP-AES and ICP-MS following decomposition using a near-total four-acid (hydrochloric, nitric, hydrofluoric, and perchloric) digestion at a temperature between 125 and 150 °C;
- mercury was determined by cold-vapor atomic absorption spectrometry (CVAAS) after dissolution in aqua regia;
- arsenic was determined by hydride-generation atomic absorption spectrometry (HGAAS) after fusion in a mixture of sodium peroxide and sodium hydroxide at 750 °C and dissolution in hydrochloric acid;
- selenium was determined by HGAAS after dissolution in a mixture of nitric, hydrofluoric, and perchloric acids; and
- total C was determined by the use of an automated carbon analyser. The sample was combusted in an oxygen atmosphere at 1370 °C to oxidize C to CO₂. The CO₂ gas was measured by a solid state infrared detector. The concentration of organic C was calculated by subtracting the amount of inorganic (carbonate) C (determined from the mineralogical data for the carbonate minerals calcite, dolomite, and aragonite) from the total C concentration.

Quality control protocols consisted of randomization of samples, by state; insertion of project standards or international reference materials at a rate of 1 per 10 project samples; and insertion of blind analytical duplicates at a rate of 1 per 80 project samples.

In addition to the chemical determinations, all samples from the soil A and C horizons were analysed by quantitative X-ray diffraction spectrometry using Rietveld refinement to determine the concentrations of the following major mineral phases: quartz, potassium feldspar, plagioclase, 10 Å clays, 14 Å clays, kaolinite, calcite, dolomite, aragonite, heulandite, analcime, hornblende, pyroxene, gibbsite, goethite, gypsum, hematite, pyrite, talc, and serpentine (Smith et al., 2014). Quality control protocols consisted of analysing standard mixtures of pure mineral phases.

Complete details of the chemical and mineralogical methods and the quality control protocols are presented in Smith et al. (2013).

3. Results and discussion

Table 1 summarizes which results per element are available for the four continental surveys described above. For many elements, analytical results for up to three different extraction methods are available. In order to keep the table as concise as possible, no numerical values are provided here; the readers are urged to check and cite the original publications. All four datasets themselves are also publicly available.

Three of the above mentioned geochemical surveys, namely those of Australia, Europe and the USA, analysed a set of exchanged project standards, allowing a level of inter-project comparison. Caritat et al. (2012) provided a first attempt at integrating continental-scale geochemical datasets to arrive at empirical, rather than largely theoretical, ‘global soil’ values. Reimann et al. (2012b) remarked that analytical quality was the single most important step required to delivering harmonised global geochemical data.

In addition to these four datasets, there exist many more multi-element geochemical datasets for a variety of areas, for a large variety of sample materials and at different sample densities and scales at many Geological Surveys or Universities. A blueprint for establishing a geochemical database at the global scale was published by Darnley et al. (1995). An overview of the history of geochemical mapping up to 2008 is provided in Garrett et al. (2008). A useful overview table of selected geochemical atlases has been presented recently by the Association of Applied Geochemists (<https://www.appliedgeochemists.org/index.php/resources/geochemical-atlases>). Some of the more prominent

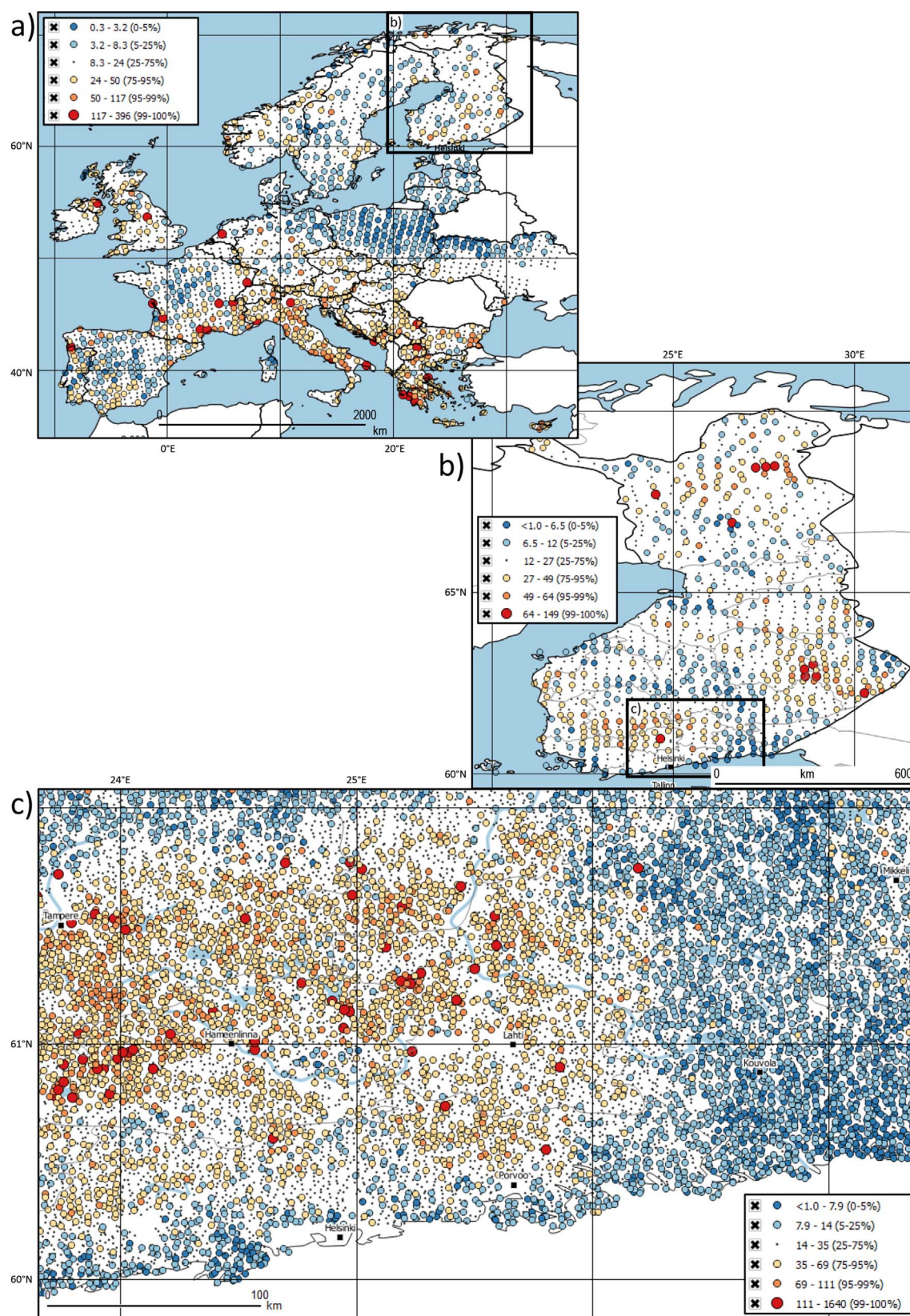


Fig. 2. Spatial distribution of aqua regia copper (Cu) concentrations in Europe and Finland at three different spatial densities: (a) one site per 2500 km² in agricultural soils (Ap horizon), 0–20 cm, < 2 mm, N = 2108 (GEMAS Project; Reimann et al., 2014a,b), (b) one site per 300 km² in basal till sediments (C horizon), ~70 cm, < 0.06 mm, N = 1057 (Geochemical Atlas of Finland[®] Geological Survey of Finland 2017; data available at: <http://en.gtk.fi/>; Koljonen, 1992), and (c) one site per 4 km² in basal till sediments (C horizon), 150–200 cm, < 0.06 mm, N = 82,060; the figure shows a detailed view of central southern Finland just north of Helsinki (Regional Till Geochemistry[®] Geological Survey of Finland 2017; data available at: <http://en.gtk.fi/>; Salminen, 1995).

recent examples of multi-element geochemical surveys, often utilizing a combination of several different sample materials at a variety of scales are listed below.

Examples of geochemical surveys from Australia include: the ~80,000 km² stream sediment geochemical survey in North Queensland (Bain and Draper, 1997); the regolith geochemical mapping program of about twenty 1:250,000-scale map sheets in Western Australia (each 1.5 degree of longitude × 1 degree of latitude in extent, or ~16,000 km²) during the late 1990's (e.g., Morris et al., 2003); the industry-sponsored laterite geochemical survey of 400,000 km² in the western Yilgarn Craton (Cornelius et al., 2008); and the multi-media geochemical survey of a 14,000 km² area in the Clarence River catchment in northeastern New South Wales (Cohen et al., 1999).

Examples of geochemical surveys from China include: the Environmental Geochemical Monitoring Network (EGMON) project in eastern and parts of western China covering ~6,000,000 km² (Xie and Cheng, 1997, 2001); the Regional Geochemistry National Reconnaissance (RGNR) project (Xie et al., 1997) covering over 5,000,000 km²; the 76 Geochemical Element Mapping (76 GEM) project (Xie et al., 2008) over ~1,000,000 km²; and the ~800,000 km² Deep Penetrating Geochemical Mapping (DEEPMAP) project (Xie et al., 2008) over covered areas at a density of ~1 site per 100 km². Xie and Cheng (2014) recently reviewed the last several decades of geochemical exploration in China. Many regional projects have also been carried out, though availability of data to the public may be restricted.

Examples of geochemical surveys from Europe include: the Forum of European Geological Surveys (FOREGS) Geochemical Atlas of Europe project (Salminen et al., 2005; De Vos et al., 2006; <http://weppi.gtk.fi/publ/foregsatlas/>); the Kola project (Reimann et al., 1998; <http://www.ngu.no/Kola/>); the Barents project (Salminen et al., 2004); the Baltic Soils Survey (BSS) project (Reimann et al., 2003); the European Groundwater Geochemistry (EGG) project (Reimann and Birke, 2010); the Geochemical Atlas of Spain (Locutura et al., 2012); the Geochemical Atlas of Cyprus (Cohen et al., 2011); the Tellus survey (Smyth, 2007; Young and Donald, 2013; https://www.bgs.ac.uk/gsn/tellus/data_licensing/index.html); and the London Earth project (Knights and Scheib, 2010; Ferreira et al., 2017; <http://www.bgs.ac.uk/gbase/londonearth.html>). Fig. 2 shows the distribution of aqua regia Cu in Europe and Finland at three different spatial densities, illustrating that the patterns are robust across various scales from one site per 2500 km² to one site per 4 km², e.g., the large Cu anomaly of southern central Finland. It also illustrates that Geological Surveys have geochemical data at a variety of densities.

Examples of geochemical surveys from USA include: the 1,700,000 km² soil and stream-sediment survey of Alaska compiled from legacy databases of the USGS and the Alaska Division of Geological and Geophysical Surveys (Lee et al., 2016); the 270,000 km² soil geochemical survey of Colorado (Smith et al., 2010); the 20,000 km² soil and stream-sediment geochemical survey of a portion of northern California (Morrison et al., 2008, 2009; Goldhaber et al., 2009); and the 1000 km² soil geochemical survey of the Denver, Colorado urban area (Kilburn et al., 2007; Smith et al., 2011b).

The above short selection of geochemical surveys demonstrates what kind of data can be expected to exist in the databases of Geological Survey organisations, usually at a range of scales (from the whole country to single cities or regions) and sample densities (from 1 site per 5000 km² to hundreds or even thousands of sites per km²). Many of the results are either published in the form of geochemical atlases or in Geological Survey reports and have as such a tendency to 'disappear' in the ever increasing flood of publications. When writing a review paper about any element(s) in the environment, such as the technologically critical elements, the above examples show that it would be prudent to check the availability of data for those elements with the Geological Surveys, which is where the most representative dataset usually can be found.

In closing, we would like to also draw attention to two international

initiatives concerned with geochemical mapping of continents and indeed the whole terrestrial globe. The first is the Commission for Global Geochemical Baselines. It was initially established in 1988 as a joint International Union for Geological Sciences/International Association of Geochemistry (IUGS/IAGC) Task Group (Smith et al., 2012) and upgraded to an IUGS Commission in 2016. Its history and, importantly, database and many more useful details can be found here: <http://www.globalgeochemicalbaselines.eu/>. The second initiative is the International Center on Global-Scale Geochemistry, recently inaugurated under the auspices of UNESCO and with considerable financial support from the government of China. This Center, headquartered in Langfang, China, aims to foster knowledge and technology for the sustainable development of global natural resources and environments; to document the global concentration and distribution of chemical elements at the Earth's surface; to educate and train the next generation of geoscientists; and to promote access to global-scale geochemical data. Although the Center's website is only being developed, preliminary details can be found here: <http://www.globalgeochemistry.com/en/>. Both the Commission and the Center are collaborating to assist many more regions and countries around the planet in acquiring geochemical datasets and atlases. Whilst already ~25% of the Earth's continental surface area is covered with geochemical data at global-scale density (i.e., mainly the four continents described herein), more will come into the public domain over coming years; watch this space!

4. Conclusion

Large and representative multi-element data sets for many different sample materials (e.g., sediment, soil) exist at Geological Surveys around the world. When setting out to write a review article on 'Element X in the environment' these datasets should be consulted and cited as they provide the all-important large-scale geochemical context. Continental-scale, fully harmonised, tightly quality controlled geochemical datasets on soils do presently exist for Australia, China, Europe and the USA. Results for a variety of chemical extractions, providing information about the (bio)availability of the elements and their likely mobility during weathering, also usually exist. Many smaller-scale, high-quality surveys exist on these and indeed other continents as well. It is suggested that an authoritative review article cannot be written without having utilized this wealth of information.

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